

# Production of Green Diesel via Solvent-aided Deoxygenation of Methyl Oleate over Bimetallic NiCo/TiO<sub>2</sub> Catalyst

Brandon Han Hoe Goh<sup>a,\*</sup>, Cheng Tung Chong<sup>a</sup>, Jo-Han Ng<sup>b</sup>

<sup>a</sup>China-UK Low Carbon College, Shanghai Jiao Tong University, Lingang, Shanghai 201306, China

<sup>b</sup>Carbon Neutrality Research Group, University of Southampton Malaysia, 79100 Iskandar Puteri, Johor, Malaysia  
 brandongohhh@gmail.com

Commercialised biodiesel, comprising of methyl esters, have large amounts of oxygenated compounds which cause low calorific value, high viscosity, poor low temperature performance and can only used in blends with petroleum-based diesel. Deoxygenation of these compounds can occur through three reaction pathways which are decarboxylation, decarbonylation, hydrodeoxygenation. The removal of oxygen can improve their fuel properties, and is heavily influenced by the presence of hydrogen (H<sub>2</sub>). However, given safety issues during transportation and storage of H<sub>2</sub>, the use of solvents to produce in-situ H<sub>2</sub> for the deoxygenation process has been suggested as an alternative. The present work attempts to investigate the addition of solvents (deionised water, methanol, ethanol, 1-propanol, 2-propanol, n-hexane and cyclohexane) on the deoxygenation of methyl oleate to enhance its fuel properties. The experiments were carried out with unreduced bimetallic NiCo impregnated onto TiO<sub>2</sub>. Incorporation of NiCo onto TiO<sub>2</sub> maintained the mesoporous nature of the support while increasing the number of strong acid sites of the catalyst, which can promote C-O bond cleavage during deoxygenation. Under hydrogen-restricted conditions, the deoxygenation is expected to occur mainly through decarboxylation and decarbonylation to produce alkanes and alkenes, with cracking to produce shorter chain methyl esters. The deoxygenation was conducted with 50 g methyl oleate, 40 g solvent, 5 wt% catalyst at 300 °C for 2 h in a pressurised nitrogen atmosphere. GCMS analysis show that the addition of 2-propanol showed the highest methyl oleate conversion (69.08 %) over other solvents, with 12.74 % selectivity for alkane formation. These results indicate the potential of solvent-aided deoxygenation of methyl esters for biofuel use.

## 1. Introduction

Biodiesels, comprised mainly of methyl esters, often face poor energy density and high corrosivity and instability issues due to the high oxygen content (Khan et al., 2019). These fatty acid methyl esters (FAME) have a similar O/C ratio to their feedstock's free fatty acids, but have a lower energy density, poorer cold flow and combustion properties (Yang et al., 2012). Catalytic hydrodeoxygenation of methyl esters can deoxygenate the feedstock to produce an upgraded green diesel, which has excellent combustion performance and low oxygen content (Yu et al., 2022). Biodiesels can be blended with petroleum diesel only to a certain extent for commercial use, but green diesel can be used without the need for blending or any engine modifications (Goh et al., 2020). Green diesel mainly consists of long-, short- and branched-chain alkanes/alkenes with an acceptable amount of aromatics (Razak et al., 2017). These deoxygenated products could potentially be used for biojet fuel blending if the required fuel properties are achieved (Zhu et al., 2022). The deoxygenation generally occurs through three reaction pathways, namely decarboxylation, decarbonylation, hydrodeoxygenation, as depicted in Figure 1. Since a majority of H<sub>2</sub> is still obtained from naphtha and natural gas steam reforming, an alternative for reduced H<sub>2</sub> use during the deoxygenation process should be investigated (Hebish et al., 2024).

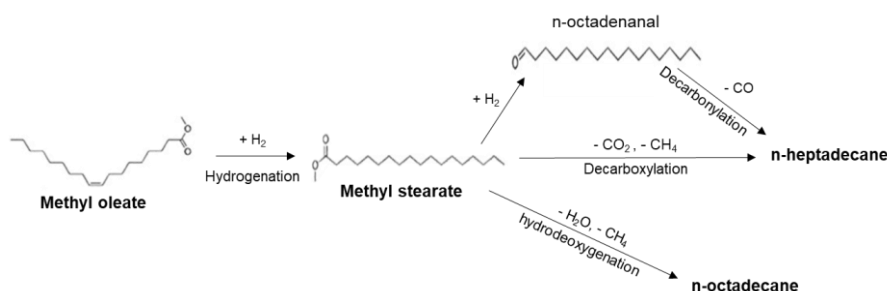


Figure 1: Deoxygenation pathway of methyl oleate adapted from (Lee and Ramli, 2013)

Typically, solvents can be added to chemical reactions to aid in stabilization, alter the reaction equilibrium constant and improve mass transfer between the reactant and product. Aqueous phase reforming (APR), also known as the in-situ adding of  $H_2$  donors for deoxygenation, has been used to circumvent the large  $H_2$  requirements. Among the studied  $H_2$  donors, methanol has shown high  $H_2$  donating capabilities (12.6 wt%), over other solvents (Ai et al., 2023). Other organic solvents such as acetone, ethyl acetate or ethanol have also been tested and found to decrease reactant viscosity, improving product selectivity while reducing the risk of catalyst deactivation (Jeon et al., 2024). The use of n-heptane in the deoxygenation of methyl stearate was also found to achieve 100 % conversion with high HDO selectivity (87 %), although comparable HDO selectivity was obtainable without solvent use (Soni et al., 2020). The excessive use of solvents may even reduce the reaction rate due to occurrence of volume expansion reactions (Pattanaik and Misra, 2017), as solvent aided deoxygenation reaction rates are often not dependent on the solvent's chemical nature, but their viscosity and boiling points.

Deoxygenation of fatty acid molecules on the metal surface needs to be done in the presence of high pressured  $H_2$  to sustain the catalytic activity, but Ni, Co, Cu and Cr have shown considerable catalytic deoxygenation activity under non- $H_2$  conditions (Phichitsurathaworn et al., 2020). Ni and Co catalysts have shown notable catalytic activity for deoxygenation due to the wide D band of these metals and energy levels near the lattice being highly advantageous for  $H_2$  adsorption and activation of oxygen containing groups (Krishnapriya et al., 2020). Under  $H_2$  restricted conditions, monometallic Ni has shown poor catalytic activity for deoxygenation of palmitic acid (Miao et al., 2016). However, the deoxygenation activity of NiO catalyst has been found to have excellent properties with high selectivity towards diesel range hydrocarbons (Khalit et al., 2021).  $Co_3O_4$  catalysts have shown significant catalytic activity for the deoxygenation of methyl oleate, but significantly drops off after a certain metal loading due to the excess particles on the support adversely affecting deoxygenation capability (Krishnapriya et al., 2020).

As of now, minimal studies have been done for the catalytic deoxygenation of methyl esters using unreduced bimetallic catalysts. Utilisation of model compounds, such as methyl oleate, rather than natural feedstocks, can simplify the reaction to further understand the conversion mechanism. In this study, an unreduced bimetallic NiCo catalyst was incorporated with  $TiO_2$  support was investigated for methyl oleate deoxygenation. The purpose of this study is to investigate the potential use of solvents to aid in the deoxygenation of methyl oleate under mild reaction conditions (300 °C  $N_2$  atmosphere stirred at 200 rpm for 6 h). NiCo catalyst was impregnated onto  $TiO_2$  support, and several solvents (water, ethanol, methanol, 1-propanol, 2-propanol, cyclohexane and n-hexane) were compared for their hydrocarbon conversion yield. The specific surface area, metal dispersion, pore distribution and acid sites of NiCo catalyst was compared to pure  $TiO_2$  support. The deoxygenation performance of each solvent-aided reaction was compared for their conversion yield and selectivity for alkanes and alkenes.

## 2. Materials and methods

Titanium (IV) oxide, nickel(II) nitrate hexahydrate, cobalt(II) nitrate hexahydrate, methyl oleate and solvents (deionised water, methanol (95 %), ethanol (95 %), 1-propanol (99 %), 2-propanol (95 %), n-hexane (95 %) and cyclohexane (95 %)) used in this study were provided by Aladdin. A GCMS analysis of the methyl oleate feedstock found that it contained a mixture of three main methyl esters, comprising 95 wt% of the feedstock, as shown in Figure 2. These include methyl oleate, methyl stearate (due to the hydrogenation of methyl oleate double bonds) and methyl pentadecanoate, a C17 methyl ester. Although the hydrogenation of methyl oleate to methyl stearate does not reduce the O/C ratio, the removal of ester groups via deoxygenation to  $C_{17}$  and  $C_{18}$  hydrocarbons is still essential for triglyceride upgrading (Krishnapriya et al., 2020).

## 2.1 Catalyst preparation and characterisation

Unreduced NiCo/TiO<sub>2</sub> catalyst were prepared based on co-impregnation conditions evaluated in our previous study (Goh et al., 2023). For determining the pore structure of the catalyst, Brunauer-Emmett-Teller (BET) method was done using a Quantachrome, Autosorb-iQ apparatus. Before analysis, the samples were degassed at a 10 °C/min heating rate to 150 °C and maintained for 6 h to remove moisture. The samples were then cooled and filled up with N<sub>2</sub> gas. SEM JOEL 6400 electron microscope (operated at 40 kV acceleration voltage) coupled with a energy dispersive X-ray spectrum (Ultim® Max EDS) was used to examine the morphology of the NiCo/TiO<sub>2</sub> catalyst and elemental mapping of Ni and Co. Ammonia temperature-programmed desorption (TPD-NH<sub>3</sub>) using Autosorb-iQ-C chemisoption instrument was used to evaluate the acid strength and acid site distribution of the catalyst. The test is done by supplying helium to the reactor at 200 mL/min for two hours to desorb any contaminants on the surface. Then the sample is cooled to 50 °C in an atmosphere with 25 ml/min flow and a composition of 8 % NH<sub>3</sub>/He for NH<sub>3</sub> adsorption, and then the gas containing probe molecules is passed in until the catalyst surface reaches adsorption saturation, and finally the temperature is increased. The gas chromatograph (HP5890) with thermal conductivity detector (TCD) detects the desorption of NH<sub>3</sub>.

## 2.2 Deoxygenation of methyl oleate

As shown in Figure 2, H<sub>2</sub> free deoxygenation of methyl oleate was done in a 500 mL autoclave. Initially, 50 g of methyl oleate, 40 g of selected solvent and 5 wt% catalyst loading was added into the reactor, before the N<sub>2</sub> gas was filled into the autoclave and purged twice. After that, the N<sub>2</sub> gas was allowed to fill the autoclave until the pressure reached the desired level. The feedstock and catalyst was magnetically stirred at 200 rpm while heated to 300 °C and maintained for 6 h. After the designated time, the vessel was allowed to cool down before being depressurised. The gaseous product was released without further analysis. Gas chromatography mass spectroscopy (GCMS) analysis was conducted onto the filtered liquid fraction using an Agilent 7890A-5975C. The samples were diluted with GC-grade dichloroethane, while the carrier gas was Argon used at a 1:10 split ratio. Oven temperature was initially held at 40 °C for 5 min. The temperature was ramped from 40 °C to 320 °C at 20 °C/min, and held for 13 min. The National Institute of Standards and Testing (NIST) library was used to identify the fraction peaks from the chromatogram. The conversion yield (measured based on remaining methyl oleate in the product) and hydrocarbon fractions (methyl esters (not including methyl oleate and methyl stearate), alcohols, alkanes and alkenes) were determined based on the chromatogram peak areas, proportional to the relative amount of each compound.

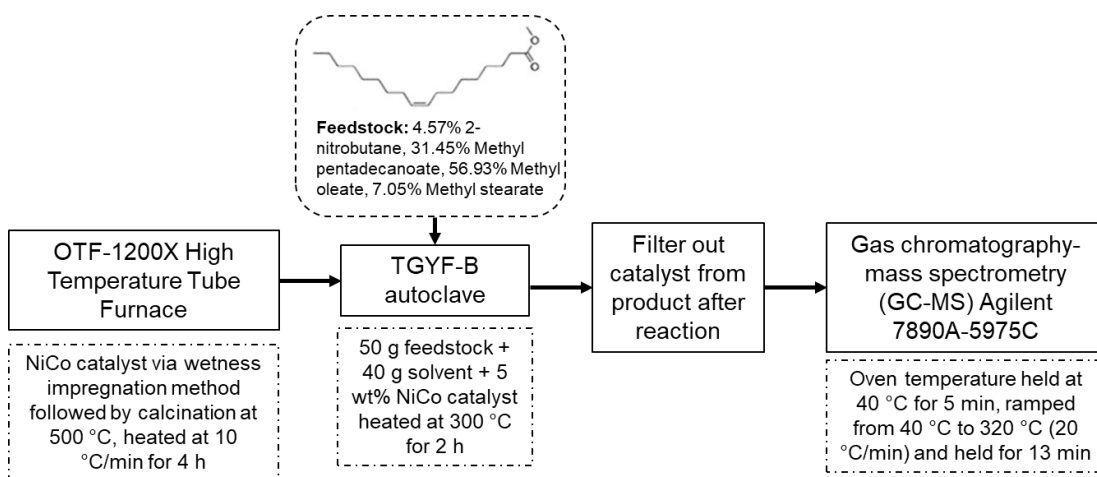


Figure 2: Chemical composition of methyl oleate and typical procedure for methyl oleate deoxygenation

## 3. Results and Discussion

From our previous study, the specific surface area (SSA) of the NiCo catalyst (77.521 mm<sup>2</sup>/g) showed slight reduction compared to pure TiO<sub>2</sub> support (84.438 mm<sup>2</sup>/g) with minimal change to the average pore diameter and pore volume (Goh et al., 2023). The N<sub>2</sub> adsorption-desorption isotherms of TiO<sub>2</sub> and NiCo/TiO<sub>2</sub> catalysts presented in Figure 3 show that both the support and catalyst have a similar type of isotherm IV with H1 hysteresis loops, which proves the mesoporous structure of the catalyst. Mesoporosity assists in catalysis due to the high surface area and ability to overcome the diffusion limitation of larger molecules (Ooi et al., 2019). Type IV isotherms indicate a mesoporous structure which proceeds through multilayer adsorption and capillary

condensation, representing disordered distributions of pore structure, size and shape of materials (Hafriz et al., 2021).

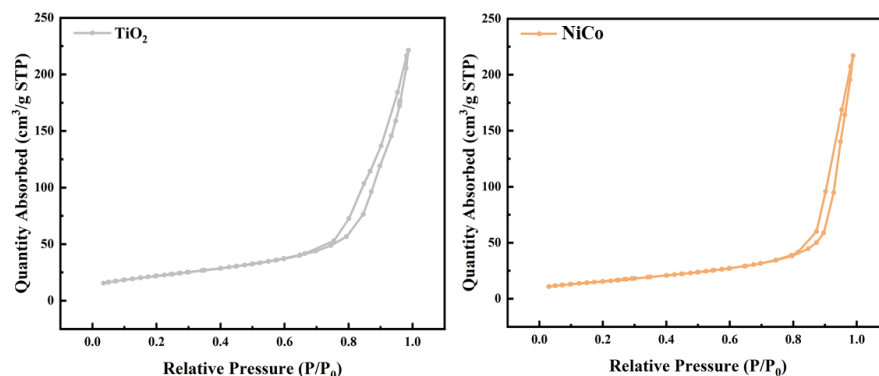


Figure 3:  $N_2$  adsorption-desorption isotherm for pure  $TiO_2$  support and bimetallic  $NiCo/TiO_2$  catalyst

The  $NiCo/TiO_2$  catalyst's SEM images paired with elemental mapping are shown in Figure 4(a). The Ni and Co particles are evenly distributed on the  $TiO_2$  surface. XRF analysis in our previous study also verified that the measured composition was similar to the actual composition (Goh et al., 2023). A high acidity promotes C-O bond cleavage during deoxygenation (Ooi et al., 2019). A comparison of the TPD- $NH_3$  for the  $NiCo/TiO_2$  catalyst and  $TiO_2$  support is also shown in Figure 4(b). The results indicate that the  $NiCo/TiO_2$  catalysts has an appropriate amount of acid sites for methyl oleate deoxygenation. The higher temperature at which the intensity peak appears indicates greater acidity, while the larger peak area means the more acid sites a catalyst has. The acidic properties of the catalyst can be interpreted as weak acid sites (below 200 °C), moderate acid sites (250–350 °C), and strong acid sites (>400 °C). Both catalysts exhibit signal peaks in the low temperature regions, while incorporation of NiCo species results in a shift of peaks from moderate to higher temperatures, indicating the formation of strong acid sites. The total acidity of the  $TiO_2$  was found to be around 1.05 mmol/g, while  $NiCo/TiO_2$  catalysts showed slight decrease in acidity to 0.67 mmol/g, which can be attributed to the decrease in SSA and possibility of metal species covering parts of the acid sites of the support. The pure  $TiO_2$  support only showed the presence of Brønsted acid sites, but there is presence of Lewis acid sites formed by the introduction of  $Co_3O_4$  and NiO onto the framework of the  $TiO_2$  support (Safa Gamal et al., 2019).

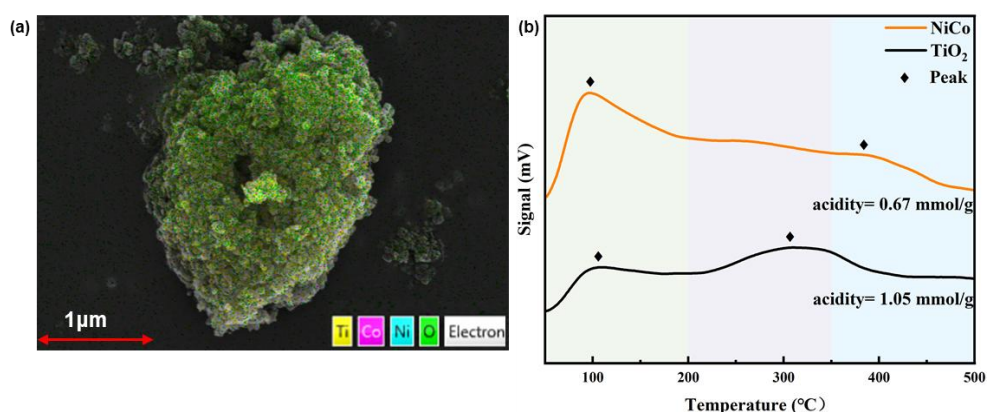


Figure 4: (a) Elemental mapping and (b) TPD- $NH_3$  of  $NiCo/TiO_2$  catalyst

Figure 5 shows the conversion and product distribution of different solvent aided deoxygenation reactions. 2-propanol showed the highest conversion yield (69.08 %), followed by 1-propanol (55.31 %), cyclohexane (55.04 %), n-hexane (44.55 %), water (31.98), ethanol (31.14 %) and methanol (31.06 %). Each run produced minimal amounts of alkenes (<2 %), while only 2-propanol (12.74 %), 1-propanol (6.49 %), cyclohexane (9.61 %) and n-hexane (8.94 %) produced significant amounts of alkane. Other solvents only produced shorter chain methyl esters, likely due to cracking at high temperatures. The mesoporous structure of the catalyst allows it to react with the methyl oleate particles on the surface and within the internal pores, providing additional adsorption and catalytic activity within the catalyst matrix (Kamaruzaman et al., 2020). The presence of strong acid sites in the

catalyst has also been found to act as the centre for cracking reactions (Safa Gamal et al., 2019). Although our previous study found that the specific surface area of the catalyst reduced with introduction of NiCo species, the active metal dispersion on the catalyst surface significantly enhanced deoxygenation performance (Goh et al., 2023). The presence of Lewis acid sites and oxygen vacancies of the TiO<sub>2</sub> allows the conversion of FAMES into carboxylate through adsorption, which are then deoxygenated through C–C breakage to form linear hydrocarbons and CO<sub>2</sub> (Prasongthum et al., 2022).

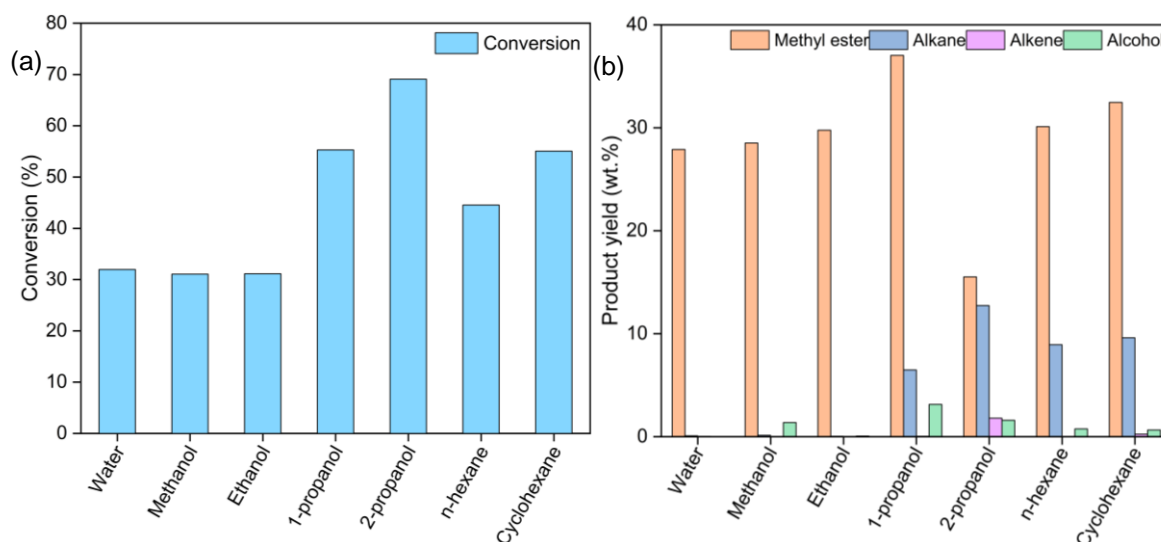


Figure 5: (a) Conversion efficiency and (b) product yield of NiCo/TiO<sub>2</sub> catalysed deoxygenation of methyl oleate aided by various solvents

Overall, the deoxygenation of methyl oleate aided by 2-propanol showed the highest conversion and alkane yield. This high catalytic activity is attributed to the introduction of Lewis acid sites, active metal dispersion and mesoporous structure of the NiCo/TiO<sub>2</sub> catalyst. The yield obtained in this study is still relatively low compared that of other studies (Goh et al., 2023; Soni et al., 2020). One possible reason for this low yield could be the reaction time, where it was reported that Co/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysed hydrodeoxygenation of methyl oleate only achieved full conversion after 10 h (Krishnapriya et al., 2020). Other reported studies involving cobalt oxide catalyst require high pressure H<sub>2</sub> (30 bar) to achieve high hydrodeoxygenation selectivity from methyl stearate (Soni et al., 2020). Given the environmental concerns and separation issues associated with organic solvents, it would be highly beneficial to investigate the trade-off between hydrogen-rich and restricted conditions during deoxygenation in terms of the hydrocarbon selectivity for a more optimal process. Alternatively, increased reaction temperature, pressure and optimised NiCo composition of the catalyst could be alternatives to improve the deoxygenation yield from methyl oleate.

#### 4. Conclusions

Solvent-aided NiCo/TiO<sub>2</sub>-catalysed deoxygenation of methyl esters is a possible option for green diesel production. In the current paper, solvent-aided deoxygenation of methyl oleate was investigated over various solvents with the use of unreduced bimetallic NiCo/TiO<sub>2</sub> catalysts. Among the investigated solvents, 2-propanol showed the highest conversion and alkane yield deoxygenation performance, followed by 1-propanol, cyclohexane and n-hexane. The high surface area, pore volume and strong acid sites of the NiCo/TiO<sub>2</sub> catalyst provided high deoxygenation activity for methyl oleate. The mesoporous structure of the catalyst overcame the diffusion limitations of larger particles. The conversion yield and hydrocarbon selectivity are far from satisfactory for use in upgraded fuel. Further investigation into the optimum reaction temperature, pressure and NiCo composition should be done to improve the deoxygenation and hydrocarbon selectivity from methyl oleate. Overall, solvent-aided deoxygenation using bimetallic NiCo/TiO<sub>2</sub> catalysts shows promise for fuel property upgrading of methyl oleate.

#### Acknowledgments

The authors graciously thank the International Excellent Young Scientists (52250610220) research fund provided by the National Natural Science Foundation of China (NSFC).

## References

- Ai L., Shi H., Chen J., 2023, In-situ deoxygenation of methyl palmitate to hydrocarbons on highly dispersed Ni-Re/TiO<sub>2</sub> catalyst in aqueous phase using methanol as a hydrogen donor, *Journal of the Energy Institute*, 109, 101265.
- Goh B.H.H., Chong C.T., Ge Y., Ong H.C., Ng J.-H., Tian B., Józsa V., 2020, Progress in utilisation of waste cooking oil for sustainable biodiesel and biojet fuel production, *Energy Conversion and Management*, 223, 113296.
- Goh B.H.H., Chong C.T., Ng J.-H., 2023, Hydrogen-free Deoxygenation of Waste Cooking Oil over Unreduced Bimetallic NiCo Catalysts for Biojet Fuel Production., *Chemical Engineering Transactions*, 106.
- Hafriz R.S.R.M., Shafizah I.N., Arifin N.A., Salmiaton A., Yunus R., Yap Y.H.T., Shamsuddin A.H., 2021, Effect of Ni/Malaysian dolomite catalyst synthesis technique on deoxygenation reaction activity of waste cooking oil, *Renewable Energy*, 178, 128-143.
- Hebish A.A., Zulkifli N.W.M., Julkapli N.M., Patah M.F.A., 2024, The impact of operating conditions on H<sub>2</sub>-free catalytic deoxygenation of triglycerides for bio-jet fuel synthesis: A step towards sustainable aviation, *Applied Catalysis O: Open*, 206926.
- Jeon K.-W., Gong J.-H., Kim M.-J., Shim J.-O., Jang W.-J., Roh H.-S., 2024, Review on the production of renewable biofuel: Solvent-free deoxygenation, *Renewable and Sustainable Energy Reviews*, 195, 114325.
- Kamaruzaman M.F., Taufiq-Yap Y.H., Derawi D., 2020, Green diesel production from palm fatty acid distillate over SBA-15-supported nickel, cobalt, and nickel/cobalt catalysts, *Biomass and Bioenergy*, 134, 105476.
- Khalit W.N.A.W., Asikin-Mijan N., Marliza T.S., Gamal M.S., Shamsuddin M.R., Saiman M.I., Taufiq-Yap Y.H., 2021, Catalytic deoxygenation of waste cooking oil utilizing nickel oxide catalysts over various supports to produce renewable diesel fuel, *Biomass and Bioenergy*, 154, 106248.
- Khan S., Kay Lup A.N., Qureshi K.M., Abnisa F., Wan Daud W.M.A., Patah M.F.A., 2019, A review on deoxygenation of triglycerides for jet fuel range hydrocarbons, *Journal of Analytical and Applied Pyrolysis*, 140, 1-24.
- Krishnapriya R., Gupta U., Soni V.K., Sharma R.K., 2020, Catalytic conversion of methyl oleate to hydrocarbons: Impact of cobalt oxide species integration in SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, *Sustainable Energy and Fuels*, 4(7), 3308-3317.
- Lee S., Ramli A., 2013, Methyl oleate deoxygenation for production of diesel fuel aliphatic hydrocarbons over Pd/SBA-15 catalysts, *Chemistry Central journal*, 7, 149.
- Miao C., Marin-Flores O., Davidson S.D., Li T., Dong T., Gao D., Chen S., 2016, Hydrothermal catalytic deoxygenation of palmitic acid over nickel catalyst, *Fuel*, 166, 302-308.
- Ooi X.Y., Oi L.E., Choo M.-Y., Ong H.C., Lee H.V., Show P.L., Juan J.C., 2019, Efficient deoxygenation of triglycerides to hydrocarbon-biofuel over mesoporous Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> catalyst, *Fuel Processing Technology*, 194, 106120.
- Pattanaik B.P., Misra R.D., 2017, Effect of reaction pathway and operating parameters on the deoxygenation of vegetable oils to produce diesel range hydrocarbon fuels: A review, *Renewable and Sustainable Energy Reviews*, 73, 545-557.
- Phichitsurathaworn P., Choojun K., Poo-arporn Y., Sooknoi T., 2020, Deoxygenation of heptanoic acid to hexene over cobalt-based catalysts: A model study for  $\alpha$ -olefin production from renewable fatty acid, *Applied Catalysis A: General*, 602, 117644.
- Prasongthum N., Suemanotham A., Sisuthog W., Thanmongkhon Y., Reubroycharoen P., Attanatho L., 2022, Production of bio-paraffin from solvent-free deoxygenation of palm biodiesel over ZrO<sub>2</sub>-supported nickel phosphide catalysts, *Applied Catalysis A: General*, 648, 118917.
- Razak N.H., Yunus N.A., Hashim H., Mansor N.N.A., 2017, Resource Planning for Sustainable Production of Tailor-Made Green Diesel, *Chemical Engineering Transactions*, 56, 727-732.
- Safa Gamal M., Asikin-Mijan N., Arumugam M., Rashid U., Taufiq-Yap Y.H., 2019, Solvent-free catalytic deoxygenation of palm fatty acid distillate over cobalt and manganese supported on activated carbon originating from waste coconut shell, *Journal of Analytical and Applied Pyrolysis*, 144, 104690.
- Soni V.K., Dhara S., Krishnapriya R., Choudhary G., Sharma P.R., Sharma R.K., 2020, Highly selective Co<sub>3</sub>O<sub>4</sub>/silica-alumina catalytic system for deoxygenation of triglyceride-based feedstock, *Fuel*, 266, 117065.
- Yang Y., Ochoa-Hernández C., de la Peña O'Shea V.A., Coronado J.M., Serrano D.P., 2012, Ni<sub>2</sub>P/SBA-15 As a Hydrodeoxygenation Catalyst with Enhanced Selectivity for the Conversion of Methyl Oleate Into n-Octadecane, *ACS Catalysis*, 2(4), 592-598.
- Yu C., Yu S., Li L., 2022, Upgraded methyl oleate to diesel-like hydrocarbons through selective hydrodeoxygenation over Mo-based catalyst, *Fuel*, 308, 122038.
- Zhu X., Xiao J., Wang C., Zhu L., Wang S., 2022, Global warming potential analysis of bio-jet fuel based on life cycle assessment, *Carbon Neutrality*, 1(1), 25.